

What is claimed is:

1. A lithographic ink composition, comprising  
a continuous phase comprising a hydrogen bonding vinyl polymer and  
an emulsified phase comprising a member selected from the group consisting of  
water, liquid polyols, and combinations thereof.
2. A lithographic ink composition according to claim 1, wherein the emulsified phase  
comprises a liquid polyol is selected from the group consisting of ethylene glycol,  
diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene  
glycol, 1,3-propanediol, dipropylene glycol, 1,4-butanediol, glycerol, and mixtures  
thereof.
3. A lithographic ink composition according to claim 1, wherein the ink composition  
includes from about 5% to about 50% of the emulsified phase by weight.
4. A lithographic ink composition according to claim 1, wherein the ink composition  
includes from about 10% to about 35% of the emulsified phase by weight.
5. A lithographic ink composition according to claim 1, wherein the ink composition  
includes from about 20% to about 30% of the emulsified phase by weight.
6. A lithographic ink composition according to claim 1, wherein the emulsified phase  
includes a weak acid or a weak base.

7. A lithographic ink composition according to claim 1, wherein the emulsified phase includes a member selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, iron(II), manganese(II), copper(II), and zinc acetates, hydroxyacetates, nitrates, sulfates, phosphates, hydrogen phosphates, hydrogen sulfates, chlorates, chlorides, bromides, iodides, and combinations thereof.

8. A lithographic ink composition according to claim 1, wherein the emulsified phase is nonaqueous.

9. A lithographic ink composition according to claim 1, wherein the emulsified phase comprises both water and a liquid polyol.

10. A lithographic ink composition according to claim 1, wherein the emulsified phase comprises a mixture of liquid polyols.

11. A lithographic ink composition according to claim 1, wherein the emulsified phase further comprises at least one solid polyol.

12. A lithographic ink composition according to claim 1, wherein the emulsified phase comprises a member selected from the group consisting of 2,3-butanediol, hexanediols, pentaerythritol, dipentaerythritol, hydroxyl-functional hyperbranched dendrimers, trimethylolethane, trimethylolpropane, neopentyl glycol, 2,2,4-trimethyl-1,3-pentanediol,

1,4-cyclohexanedimethanol, hydrogenated bisphenol A, compounds having one hydroxyl group and up to about 18 carbon atoms, and combinations thereof.

13. A lithographic ink composition according to claim 1, wherein the emulsified phase comprises a member selected from the group consisting of citric acid, tartaric acid, tannic acid, and combinations thereof.

14. A lithographic ink composition according to claim 1, wherein the emulsified phase comprises triethanolamine.

15. A lithographic ink composition according to claim 1, wherein the emulsified phase comprises from about 0.01 weight percent to about 2 weight percent of a weak acid or a weak base.

16. A lithographic ink composition according to claim 1, wherein the emulsified phase comprises from about 0.01 weight percent to about 0.5 weight percent of magnesium nitrate.

17. A lithographic ink composition according to claim 1, wherein the emulsified phase comprises a water soluble polymer.

18. A lithographic ink composition according to claim 1, wherein the emulsified phase comprises a member selected from the group consisting of poly(vinyl pyrrolidone), poly(vinyl alcohol), poly(ethylene glycol), and combinations thereof.

19. A lithographic ink composition according to claim 1, wherein the hydrogen bonding vinyl polymer comprises hydrogen bonding groups selected from the group consisting of carboxylic acid groups, carboxylic anhydride groups, primary amine groups, amine groups having N-alkyl substituents of three or fewer carbon atoms, primary amide groups, amide groups having N-alkyl substituents of three or fewer carbon atoms, ester groups having pendant alkyl groups of three or fewer carbon atoms,  $\beta$ -hydroxyl ester groups, hydroxyl groups, sulfur-containing groups, phosphorous-containing groups, acetoacetate groups, and combinations thereof.

20. A lithographic ink composition according to claim 1, wherein the hydrogen bonding vinyl polymer comprises primary amine groups, amine groups having N-alkyl substituents of three or fewer carbon atoms, or combinations thereof.

21. A lithographic ink composition according to claim 1, wherein the hydrogen bonding vinyl polymer comprises primary amide groups, amide groups having N-alkyl substituents of three or fewer carbon atoms, or combinations thereof.

22. A lithographic ink composition according to claim 1, wherein the hydrogen bonding vinyl polymer comprises hydroxyl groups.

23. A lithographic ink composition according to claim 1, wherein the hydrogen bonding vinyl polymer comprises carboxylic acid groups, carboxylic anhydride groups, or combinations thereof.

24. A lithographic ink composition according to claim 1, wherein the hydrogen bonding vinyl polymer comprises ester groups having pendant alkyl groups of three or fewer carbon atoms,  $\beta$ -hydroxyl ester groups, or combinations thereof.

25. A lithographic ink composition according to claim 1, wherein the hydrogen bonding vinyl polymer comprises sulfur-containing groups.

26. A lithographic ink composition according to claim 1, wherein the hydrogen bonding vinyl polymer comprises hydrogen bonding groups selected from the group consisting of sulfonic acid groups, sulfonamide groups, sulfoxide groups, sulfone groups, mercapto groups, phosphoric acid groups, phosphate groups, phosphonamide groups, and combinations thereof.

27. A lithographic ink composition according to claim 1, wherein the hydrogen bonding vinyl polymer comprises vinyl alcohol monomeric units.

28. A lithographic ink composition according to claim 22, wherein the emulsified phase includes a weak base.

29. A lithographic ink composition according to claim 1, wherein the hydrogen bonding vinyl polymer comprises a combination of different hydrogen bonding groups.

30. A lithographic ink composition according to claim 1, wherein the hydrogen bonding groups of the hydrogen bonding vinyl polymer function as hydrogen donating groups.

31. A lithographic ink composition according to claim 1, wherein the hydrogen bonding groups of the hydrogen bonding vinyl polymer function as hydrogen accepting groups.

32. A lithographic ink composition according to claim 1, wherein the hydrogen bonding groups of the hydrogen bonding vinyl polymer function as both hydrogen donating and hydrogen accepting groups.

33. A lithographic ink composition according to claim 30, wherein the emulsified phase includes a weak base.

34. A lithographic ink composition according to claim 31, wherein the emulsified phase includes a weak acid.

35. A lithographic ink composition according to claim 1, wherein the hydrogen bonding vinyl polymer has an equivalent weight, based on hydrogen bonding groups, of at least about 1800 grams per equivalent.

36. A lithographic ink composition according to claim 1, wherein the hydrogen bonding vinyl polymer has an equivalent weight, based on hydrogen bonding groups, of up to about 20,000 grams per equivalent.

37. A lithographic ink composition according to claim 1, wherein the hydrogen bonding vinyl polymer has an equivalent weight, based on hydrogen bonding groups, of from about 2200 grams per equivalent to about 7200 grams per equivalent.

38. A lithographic ink composition according to claim 1, wherein the hydrogen bonding vinyl polymer comprises acetoacetate groups.

39. A lithographic ink composition, comprising  
a hydrophobic, continuous phase comprising a solution of a branched, hydrogen bonding vinyl polymer and  
an emulsified phase comprising a member selected from the group consisting of water, liquid polyols, and combinations thereof.

40. A lithographic ink composition according to claim 39, wherein the emulsified phase comprises a liquid polyol is selected from the group consisting of ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, 1,3-propanediol, 1,4-butanediol, glycerol, and mixtures thereof.

41. A lithographic ink composition according to claim 39, wherein the ink composition includes from about 5% to about 50% of the emulsified phase by weight.

42. A lithographic ink composition according to claim 39, wherein the ink composition includes from about 10% to about 35% of the emulsified phase by weight.

43. A lithographic ink composition according to claim 39, wherein the emulsified phase includes a member selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, iron(II), manganese(II), copper(II), and zinc acetates, hydroxyacetates, nitrates, sulfates, phosphates, hydrogen phosphates, hydrogen sulfates, chlorates, chlorides, bromides, iodides, and combinations thereof..

44. A lithographic ink composition according to claim 39, wherein the emulsified phase is nonaqueous.

45. A lithographic ink composition according to claim 39, wherein the emulsified phase comprises both water and a liquid polyol.



46. A lithographic ink composition according to claim 39, wherein the emulsified phase comprises a mixture of liquid polyols.

47. A lithographic ink composition according to claim 39, wherein the emulsified phase further comprises at least one solid polyol.

48. A lithographic ink composition according to claim 39, wherein the emulsified phase comprises a member selected from the group consisting of 2,3-butanediol, hexanediols, pentaerythritol, dipentaerythritol, hydroxyl-functional hyperbranched dendrimers, trimethylolethane, trimethylolpropane, neopentyl glycol, 2,2,4-trimethyl-1,3-pentanediol, 1,4-cyclohexanedimethanol, hydrogenated bisphenol A, compounds having one hydroxyl group and up to about 18 carbon atoms, and combinations thereof.

49. A lithographic ink composition according to claim 39, wherein the emulsified phase comprises from about 0.01 weight percent to about 2 weight percent of a weak acid or a weak base.

50. A lithographic ink composition according to claim 39, wherein the emulsified phase comprises a wetting agent.

51. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer comprises hydrogen bonding groups selected from the group consisting of carboxylic acid groups, carboxylic anhydride groups, primary amine

groups, amine groups having N-alkyl substituents of three or fewer carbon atoms, primary amide groups, amide groups having N-alkyl substituents of three or fewer carbon atoms, ester groups having pendant alkyl groups of three or fewer carbon atoms,  $\beta$ -hydroxyl ester groups, hydroxyl groups, sulfur-containing groups, phosphorous-containing groups, acetoacetate groups, and combinations thereof.

52. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer comprises primary amine groups, amine groups having N-alkyl substituents of three or fewer carbon atoms, or combinations thereof.

53. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer comprises primary amide groups, amide groups having N-alkyl substituents of three or fewer carbon atoms, or combinations thereof.

54. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer comprises hydroxyl groups.

55. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer comprises carboxylic acid groups, carboxylic anhydride groups, or combinations thereof.

56. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer comprises ester groups having pendant alkyl groups of three or fewer carbon atoms,  $\beta$ -hydroxyl ester groups, or combinations thereof.

57. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer comprises sulfur-containing groups.

58. A lithographic ink composition according to claim 39, wherein the emulsified phase includes a weak base.

59. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer comprises a combination of different hydrogen bonding groups.

60. A lithographic ink composition according to claim 39, wherein the hydrogen bonding groups of the hydrogen bonding vinyl polymer function as hydrogen donating groups.

61. A lithographic ink composition according to claim 39, wherein the hydrogen bonding groups of the hydrogen bonding vinyl polymer function as hydrogen accepting groups.

62. A lithographic ink composition according to claim 39, wherein the hydrogen bonding groups of the hydrogen bonding vinyl polymer function as both hydrogen donating and hydrogen accepting groups.

63. A lithographic ink composition according to claim 60, wherein the emulsified phase includes a weak base.

64. A lithographic ink composition according to claim 61, wherein the emulsified phase includes a weak acid.

65. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer has an equivalent weight, based on hydrogen bonding groups, of at least about 1800 grams per equivalent.

66. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer has an equivalent weight, based on hydrogen bonding groups, of up to about 20,000 grams per equivalent.

67. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer has an equivalent weight, based on hydrogen bonding groups, of from about 2200 grams per equivalent to about 7200 grams per equivalent.

68. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer is polymerized using at least one monomer having two or more polymerizable ethylenically unsaturated bonds.

69. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer is polymerized using divinylbenzene.

70. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer is polymerized using at least about 0.008 equivalents per 100 grams of monomer polymerized of at least one monomer having two or more polymerizable ethylenically unsaturated bonds.

71. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer is polymerized using from about 0.012 to about 0.08 equivalents per 100 grams of monomer polymerized of at least one monomer having two or more polymerizable ethylenically unsaturated bonds.

72. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer is polymerized using from about 0.016 to about 0.064 equivalents per 100 grams of monomer polymerized of at least one monomer having two or more polymerizable ethylenically unsaturated bonds.

73. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer is polymerized using at least about 0.004 equivalents per 100 grams of monomer polymerized of each of two monomers having mutually reactive groups in addition to an ethylenically unsaturated polymerizable bond.

74. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer has been branched with a member selected from the group consisting of aluminum gellants, alkoxytated titanates, alkoxytated zirconates, and combinations thereof.

75. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer has been branched with a member selected from the group consisting of aluminum acetoacetate, aluminum triisopropoxide, aluminum tris-sec-butoxide, aluminum diisopropoxide aceto ester, aluminum oxyacrylate, and combinations thereof.

76. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer has a number average molecular weight of at least about 1000 and a weight average molecular weight of at least about 30,000.

77. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer has a weight average molecular weight of at least about 100,000.

78. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer has a polydispersity of at least about 15.

79. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer has a polydispersity of at least about 50.

80. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer has a polydispersity of from about 15 to about 1000.

81. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer has a polydispersity of from about 50 to about 800.

82. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer has a theoretical glass transition temperature above room temperature.

83. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer has a theoretical glass transition temperature of at least about 60°C.

84. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer has a theoretical glass transition temperature from about 50°C to about 125°C.

85. A lithographic ink composition according to claim 39, wherein the continuous phase comprises a further material selected from the group consisting of polyesters, alkyds, phenolics, rosins, cellulosics, rosin-modified phenolics, phenolic-modified rosins, hydrocarbon-modified rosins, maleic-modified rosins, fumaric-modified rosins, hydrocarbon resins, polyamides, vinyl polymers that do not hydrogen bond with the emulsified phase, and combinations thereof.

86. A lithographic ink composition according to claim 85, wherein the further material is included in an amount of from about 1 part by weight up to about 100 parts by weight for each part by weight of the hydrogen bonding vinyl polymer.

87. A lithographic ink composition according to claim 85, wherein the further material is included in an amount of from about 3 part by weight up to about 50 parts by weight for each part by weight of the hydrogen bonding vinyl polymer.

88. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer is polymerized using at least about 15% by weight of acrylic esters having at least six carbons in the alcohol portion, based on total monomer weight.

89. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer is polymerized using from about 15% to about 30% by weight of



acrylic esters having from about eight to about twenty carbons in the alcohol portion, based on total monomer weight.

90. A lithographic ink composition according to claim 39, wherein the hydrogen bonding vinyl polymer is polymerized using from about 50% to about 80% by weight of styrene, based on total monomer weight.

91. A lithographic ink composition, comprising  
a hydrophobic, continuous phase comprising a solution of a branched, hydrogen bonding vinyl polymer and  
an emulsified phase having, as Hansen's solubility parameter values, a dispersion parameter value of at least about 6, a polarity parameter value of at least about 4, and a hydrogen bonding parameter value of at least about 10.

92. A lithographic ink composition according to claim 91, wherein the dispersion parameter value is from about 8 to about 9, the polarity parameter value is from about 5 to about 8, and the hydrogen bonding parameter value is from about 12 to about 20.

93. A lithographic ink composition, comprising  
a continuous phase comprising a vinyl polymer comprising primary amide groups, amide groups having N-alkyl substituents of three or fewer carbon atoms, or combinations thereof, wherein the vinyl polymer has a polydispersity of at least about 15; and

an emulsified phase comprising a member selected from the group consisting of water, liquid polyols, and combinations thereof.

94. A lithographic ink composition according to claim 93, wherein the emulsified phase comprises a liquid polyol is selected from the group consisting of ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, 1,3-propanediol, dipropylene glycol, and mixtures thereof.

95. A lithographic ink composition according to claim 93, wherein the ink composition includes from about 5% to about 50% of the emulsified phase by weight.

96. A lithographic ink composition according to claim 93, wherein the ink composition includes from about 10% to about 35% of the emulsified phase by weight.

97. A lithographic ink composition according to claim 93, wherein the ink composition includes from about 20% to about 30% of the emulsified phase by weight.

98. A lithographic ink composition according to claim 93, wherein the emulsified phase includes a weak acid or a weak base.

99. A lithographic ink composition according to claim 93, wherein the emulsified phase includes a member selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, iron(II), manganese(II), copper(II), and zinc acetates,

hydroxyacetates, nitrates, sulfates, phosphates, hydrogen phosphates, hydrogen sulfates, chlorates, chlorides, bromides, iodides, and combinations thereof.

100. A lithographic ink composition according to claim 93, wherein the emulsified phase is nonaqueous.

101. A lithographic ink composition according to claim 93, wherein the vinyl polymer further comprises ester groups having pendant alkyl groups of three or fewer carbon atoms,  $\beta$ -hydroxyl ester groups, or combinations thereof.

102. A lithographic ink composition according to claim 101, wherein the vinyl polymer has an equivalent weight, based on total amide and ester groups, of from about 2200 grams per equivalent to about 7200 grams per equivalent.

103. A lithographic ink composition according to claim 102, wherein the amide groups are obtained by copolymerizing N,N-dimethyl acrylamide and the ester groups are obtained by copolymerizing methyl methacrylate.

104. A lithographic ink composition according to claim 93, wherein the vinyl polymer has a number average molecular weight of between about 1000 and about 15,000 and a weight average molecular weight of at least about 100,000.

105. A lithographic ink composition according to claim 93, wherein the continuous phase includes a further material selected from the group consisting of polyester resins, hydrocarbon resins, alkyd resins, phenolic resins, rosins, cellulosic resins, and modifications thereof, and mixtures thereof.

106. A lithographic ink composition according to claim 105, wherein the further material is less hydrophilic than the acid-functional vinyl polymer.

107. A method of making a lithographic printing ink, comprising a step of combining a first composition comprising an amide-functional, hydrogen bonding vinyl polymer and a second composition comprising a member selected from the group consisting of water, liquid polyols, and combinations thereof, whereby a printing ink is formed having as a continuous phase the first composition and as a discontinuous phase the second composition.

108. A lithographic ink composition according to claim 93, wherein the emulsified phase comprises water.

109. A lithographic ink composition according to claim 93, wherein the emulsified phase further comprises a member selected from the group consisting of solid polyol compounds, solid polyol oligomers, and compounds having one hydroxyl group and up to about 18 carbon atoms.

110. A printing method, comprising a step of printing a substrate by lithographic printing using as a single fluid lithographic ink the ink according to claim 1.

111. A printing method, comprising a step of printing a substrate by lithographic printing using as a single fluid lithographic ink the ink according to claim 93.

112. A printing method, comprising a step of printing a substrate by lithographic printing using as a single fluid lithographic ink the ink according to claim 93.